# Effects of heating on the emanation rates of radon-222 from a suite of natural minerals

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## Abstract

The emanating power of radon provides information on the internal structure of a mineral and the radiation damage caused by the decay of $^{238}$U, $^{235}$U and $^{232}$Th (and their daughters) that are present in the mineral. The concentration of $^{222}$Rn in groundwater is primarily controlled by the concentration of U and Th in the underlying rocks, as well as the emanation coefficient for that particular rock. The variations in the emanation coefficient for $^{222}$Rn caused when subsurface rocks are subjected to tectonic forces results in changes in $^{222}$Rn in groundwater. Increased emanation rates of radon from a mineral grain can potentially alter the $^{238}$U–$^{206}$Pb, $^{235}$U–$^{207}$Pb and $^{232}$Th–$^{208}$Pb chronological clocks.

We have measured radon emanation coefficients on a suite of minerals comprised of one oxide (uraninite), three silicates (thorite, zircon, and cerite) and one phosphate (monazite) at room temperature and after heating at 200 C and 600 C. Annealing of some of the nuclear tracks within a mineral significantly reduces the emanation rates of radon in these minerals, suggesting that the tracks created by decay events serve as conduit pathways for the release of $^{222}$Rn. Higher emanation rates of $^{222}$Rn from mineral grains that are surrounded by liquid as compared to air indicate that a major portion of the escaping $^{222}$Rn in air gets embedded into adjacent mineral grains and/or opposite walls of a pore.
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## 1. Introduction

In certain parts of the United States, emanation rates of $^{222}$Rn and its entry into homes have been a serious concern to public health for a number of years. The proportion of the $^{222}$Rn released to the total amount of radon produced is termed the radon emanation coefficient. In literature, several terms including 'emanating power,' 'coefficient of emanation,' 'escape ratio,' escape-to-production ratio,' and 'percent emanation,' have been used to describe this parameter (Tanner, 1980). Radon in the environment, derived mainly from rocks and soils, accounts for over half of a typical individual's exposure

to radiation (NCRPM, 1987; Greeman and Rose, 1996). The emanation rate of radon is an important parameter on the release of radon to air. Concentrations of $^{222}$Rn in groundwater and air have been utilized as tracers in earth sciences for such applications as locating subsurface uranium deposits (Levinson et al., 1982), detecting long-distance migration of gases within the earth (Fleischer and Mogrocampero, 1985), predicting earthquakes (e.g., Fleischer and Mogrocampero, 1985; Wakita et al., 1991; Igarashi et al., 1995; Whitehead and Lyon, 1999), and identifying the existence of subsurface hydrocarbon deposits (Fleischer and Turner, 1984). When a $^{226}$Ra atom undergoes radioactive decay to $^{222}$Rn, the recoil energy is B 100 keV and in common minerals the recoil range is B 40 nm (e.g., Amin and Rama, 1986; 35 nm in clays, 95 nm in water and 64 000 nm in air, Semkow, 1990). Such a short range

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implies that only those $^{226}$Ra atoms that lie extremely close to the surface can contribute to emanation. $^{222}$Rn atoms in the deeper region of a crystal are not available without the development of a large internal surface area that could result from weathering, corrosion from chemical reactions or intensive fracturing on a microscopic scale. From a study on the diffusion of thoron ($^{220}$Rn), Rama and Moore (1990) proposed that zones of submicron porosity in minerals run both along the grain boundaries and across the grains. The submicron porosity varies widely depending on the mineral and rock type, from 10% to 80%. Emanation coefficients in the range of a few percent to B 40%, that are common in rocks and minerals, have been reported (e.g., Rama and Moore, 1984; Amin and Rama, 1986; Landa, 1987; Morawska and Phillips, 1993; Przylibski, 2000).

The internal porosity and radiation damage within a mineral largely affect the radon emanation rates. Thus, emanation rates of $^{222}$Rn provide information on the internal structure of minerals. The recoil length is a measure of the internal structure, stability and damage within a mineral, under the assumption that the $^{238}$U and its daughter products are distributed uniformly. For several of the rock-forming minerals, $^{238}$U and $^{232}$Th are located along grain boundaries in accessory minerals (e.g., Krishnaswami and Seidemann, 1988); however, in U-and Th-rich minerals, they are primarily distributed uniformly within the crystal structure (except zircon and monazite). Internal damage to the mineral structure caused by radioactive decay could significantly alter the rates of diffusion of Rn and dissolution of a mineral and thereby affect the subsequent radon emanation coefficient (REC, ratio of $^{222}$Rn released to the total amount produced, expressed normally as a percentage of the total). Therefore, the changes in the REC values for a given mineral can provide valuable information on changes in internal structure (mainly damage caused by fission, alpha and recoil tracks) of that mineral. The resulting accelerated release of $^{222}$Rn in a mineral over extended periods of time could significantly alter the U–Pb chronological clock of that mineral.

The relative importance of nuclear tracks (alpha, recoil and fission) on radon emanation is not known, although it is believed to be an important factor. By heating many minerals at > 600 C, a major portion of the nuclear tracks can be annealed and the relative importance of these tracks to Rn release rates can be deciphered. For example, fission tracks are annealed at temperatures higher than 200 7 50 C, which is lower than the temperature required to anneal a-recoil tracks (Murakami et al., 1991). Additionally, a comparison of the radon release rates in annealed minerals placed inside a liquid with those placed in air will provide information on the importance of the emanating medium to the accumulation of radon. In this article, we investigate the changes in REC values when a suite of minerals are subjected to heating and immersed inside a liquid. The release of radon from rocks and minerals has direct bearing on the reliability of U–Pb ages. To our knowledge, this is the first systematic attempt to determine the variations of REC when the nuclear tracks (both recoil and alpha) are annealed, as well as the variations as a function of grain-sizes and medium surrounding the mineral grains.

## 2. Materials and Methods

We examined five natural minerals for this investigation: zircon, monazite, uraninite, cerite, and thorite. The sample description, locality, specific gravity, estimated ages and mineralogical composition of these samples are given in Table 1. To determine if there is any variation in REC values as a function of grain size, a monazite sample was crushed and dry-sieved to five size ranges: o 63, 63–250, 250–500, 500–1000mm, and 1–2 mm. The natural variability in the radon emanation coefficient was determined by measuring the $^{222}$Rn emanation coefficient 3–4 times for each of the fractions. The $^{222}$Rn emanation coefficients and the coefficient of variations are given in Table 2. It was observed that the differences in emanation coefficients of $^{222}$Rn between 63–250mm and 1–2 mm size ranges were small and therefore the heating experiments were only carried out on the smallest and largest size fractions, namely o 63mm and 1–2 mm.

Each of the minerals was crushed and dry-sieved to the two size fractions (o 63 and 500–1000mm), and the samples were subsequently subjected to various degrees of heating. Sample sizes (5–30g) were taken based on the expected measurable activity as found by gamma-ray counting of the powdered samples. The emanation coefficients were determined on unheated minerals as well as on minerals that were subjected to heating at 100 C for 48h, 200 C for 48 h and 600 C for 6 h. After heating, the minerals were allowed to cool and were placed in 500 ml Pyrex gas-washing bottles. The bottles were then flushed with helium and sealed for 7–24 days before radon measurements were carried out.

The radon was extracted from the sample bottle on to an activated charcoal column using the Rn extraction system and then, subsequently transferred to a counting cell using the transfer board (Mathieu et al., 1988). The samples were counted on the Pylon AB-5 portable radiation monitor. The rate of emanation for each mineral was calculated for each temperature in terms of atoms emanated per gram per minute. The U and Th concentrations were measured by counting a known weight of the sample in a 10-ml gamma counting vial in a high-purity Ge-Well detector (Canberra) coupled to a Canberra InSpector multi-channel analyzer. The active volume of the crystal was 179cm$^3$. There was no peak

Table 1
Mineral samples used for analysis

| Mineral | Locality | Specific gravity | Crystal system | Chemical formula | Estimated age (billion years) | Mineralogical group |
|---------|----------|------------------|----------------|------------------|------------------------------|---------------------|
| Monazite | Petaca District, New Mexico | 4.6–5.4 | Monoclinic | $(Ce, La, Nd, Th)PO_4$ | 1.4 7 0.2 | Rare earth phosphate |
| Thorite | Tory Hill, Ontario | 5.3 | Tetragonal | $(Th, U) SiO_4$ | 1.0 7 0.2 | Thorium uranium silicate |
| Uraninite | Fission Mine, Wilberforce, Ontario | 7.5–9.7 | Isometric | $UO_2$ | 1.0 7 0.2 | Uranium oxide |
| Zircon | Goias, Brazil Tory Hill, Ontario | 4.7 | Tetragonal | $ZrSiO_4$ | 2.9 7 0.2 | Zirconium silicate |
| Cerite | Boulder Co., Colorado | 4.7–4.9 | Hexagonal | $(Ce, Ca)_9(Mg,Fe)Si_7(O, OH, F)_{28}$ | 1.0 7 0.2 | Silicate, neosilicates |

Table 2
Reproducibility and coefficient of variations of $^{222}$Rn emanation rate on Monazite sample at room temperature

| Grain size (mm) | Number of observations | $^{222}$Rn emanation rate (atoms $g^{-1} m^{-1}$)[a] | Range | Coefficient of variation (%) |
|-----------------|------------------------|----------------------------------|-------|------------------------------|
| o 63 | 4 | 21.7 7 2.1 | 20.2–24.7 | 9.6 |
| 63–250 | 4 | 12.8 7 2.9 | 10.4–17.0 | 22.5 |
| 250–500 | 4 | 10.8 7 1.9 | 8.29–13.1 | 18.4 |
| 500–1000 | 4 | 8.7 7 1.4 | 7.90–10.9 | 16.8 |
| 1000–2000 | 3 | 10.4 7 0.7 | 9.81–11.2 | 6.7 |

[a] The errors reported are the standard deviation on the measurements. The propagated counting error on the emanation rates arising from counting statistics, errors associated with the counting cell efficiencies, and the errors associated with the activity of the sample, is less than 5%.

background in any of the regions of interest (46.5 keV for $^{210}$Pb, 63 keV for $^{234}$Th, 351 and 609 keV for $^{226}$Ra and 338 and 911 keV for $^{228}$Ra). The Peak/Compton ratio at 1.332 keV was 56.6:1. The Full-Width at Half-Maxima at 0.122 and 1.332 MeV were 1.26 and 1.99 keV, respectively. The matrix densities of the standard and sample were quite comparable, and hence the self-absorption corrections were quite comparable, and were not applied. The gamma-ray detector was calibrated with solid standards (RGU-1 and RGTh-1) obtained from the International Atomic Energy Agency (IAEA) for $^{210}$Pb, $^{234}$Th and $^{226}$Ra (RGU-1 standard) and $^{228}$Ra (RGTh-1 standard). The ratios of the disintegrations per minute (dpm) to counts per minute (cpm) were obtained for various geometries. The

conversion factor (dpm/cpm) was used to calculate the activities of $^{226}$Ra and $^{228}$Ra. The errors associated with the dpm/cpm conversion factors were always less than 1%. The propagated errors (errors arising from the calibration of the detector and errors associated with the sample counting) on the activities of the samples were less than 2%.

## 3. Results and Discussion

### 3.1. Radon emanation in air

The coefficient of variation on the radon emanation rates for various grain sizes of monazite varied between

7% and 23% (Table 2). Although the propagated errors (errors arising from counting statistics including background subtraction and detector calibration) on the $^{222}$Rn and $^{226}$Ra concentrations were less than 5%, the coefficient of variation is high, most likely due to the variability in experimental conditions, particularly when the gas washing bottle was filled with He gas. We filled the gas-washing bottle containing the sample with He to 1 atm pressure using a standard gauge mounted on the Rn extraction board, however some small pressure deviations could have occurred. This small difference in pressure could result in varying radon emanation rates from minerals. It is well known that a small differential between the atmospheric pressure and the pressure inside a house is the cause for the indoor radon problem in colder regions such as Alaska. In addition, Tanner (1980) reported that an Apollo 14 sample showed up to a several fold increase in apparent emanating power when the pressure was increased to 1 atm.

The radon emanation rate in the o 63 mm fraction for monazite is distinctly higher than the other 4 fractions (Table 2). However, there is no difference in the emanation rate between 250–500 and 1000–2000 mm size ranges. The concentrations of $^{238}$U (measured via $^{226}$Ra) and $^{232}$Th (via $^{228}$Ac) in the ground bulk mineral samples as determined by gamma-ray spectrometry are given in Table 3. When $^{238}$U is homogenously distributed in minerals, the leakage of $^{222}$Rn by recoil (assuming no diffusion) from the outer 50 nm layer (corresponding to the recoil range of $^{222}$Rn resulting from the decay of $^{226}$Ra) of mm-size grains is estimated to be less than 0.01% (since the volume of the outer 50 nm layer in a 63 mm grain size is less than 0.01%). The diffusion length (L) of B 0.02 m is estimated for $^{222}$Rn from the relationship: L B (D/l)$^{1/2}$ where D is the diffusion coefficient of radon in solids, $10^{-5}$ cm$^2$ s$^{-1}$ (Tanner, 1980), and l is the decay constant of $^{222}$Rn. This diffusion length is significantly larger than the

largest crystal size range used for this experiment, and thus the emanation of radon is expected to be independent of the grain size. For example, for spherical, isotropic grains of $SiO_2$, the typical probability of $^{222}$Rn escape ranges from about 1.0 for grains of less than 0.1 mm diameter to about 0.54 for grains of 0.9 mm diameter (Tanner, 1978). It has been reported that the leakage of thoron (half-life = 55.6 s) is nearly the same as that of radon, suggesting that transport time within the grain has to be quite short, of the order of seconds (Rama and Moore, 1984). In addition, Amin and Rama (1986) showed that the radon emanation coefficient on a 30 cm ∟ 30 cm ∟ 30 cm cube of granite is the same as for a 1–2 mm granite and they proposed the presence of openings inside natural crystalline minerals that provide a large internal area. The suggested openings are very narrow (nm range) and are interconnected to form an extensive network.

The radon emanation coefficient in the four minerals measured at room temperature varied over an order of magnitude, from 0.53% in uraninite to 5.38% in thorite (Table 4). The REC for uraninite is significantly lower than the value of 12–15% reported by Morawska and Phillips (1993), and the difference is attributed to the differences in the ages of the minerals and inner properties of the sample. This range of values can be compared to the values published in literature: 7.6% to 33% on 68 disaggregated soil samples representative of the eastern USA (Greeman and Rose, 1996); 7% to 41% for crystalline rocks of the Sudety Mountains (SW Poland), (Przylibski, 2000); 0.03% to 18% in a variety of natural rocks and minerals including monazite and zircon, (Rama and Moore, 1984); and 4% to 12% for ore and tailings of U (Landa, 1987).

The radon emanation rates and emanation coefficients for the four minerals are given in Table 4. The comparison of the REC values for emanation into gas or liquid before and after heating the minerals are given in Table 5. From the data reported in Tables 4 and 5, the following observations can be made: (1) With the exception of 1–2 mm sized zircons, the radon emanation coefficient is lowest for all annealed minerals for release into air, and has been reduced 55–75% at 600 C as compared to unannealed minerals. In this text, annealed refers to minerals that have been heated to 600 C causing complete removal of all the fission tracks and partial removal of the recoil and alpha tracks. Murakami et al. (1991) heated zircons for 2 days at 750 C and could detect no evidence of annealing of alpha recoil damage. The kinetics of annealing, including the extent of radiation damage and duration of heating as well as maximum temperature, is important in the elimination of radiation damage. Except for the mineral uraninite, the REC is highest for all minerals at room temperature; (2) For monazite, zircon and uraninite, the REC values follow the trend: 200 C > 100 C > 600 C; (3) The

Table 3
Activities of $^{238}$U and $^{232}$Th in the ground bulk mineral samples as determined by gamma spectrometry

| Mineral | $^{232}$Th (via $^{228}$Ac) dpm g$^{-1}$ | $^{238}$U (via $^{226}$Ra) dpm g$^{-1}$ |
|---|---|---|
| Monazite | 24 477 7 266 | 1058 7 22 |
| Zircon | 273 7 3 | 3008 7 28 |
| Thorite | 52 119 7 547 | 6263 7 95 |
| Cerite | 859 7 10 | 2563 7 30 |
| Uraninite | 22 604 7 439 | 349 740 7 4150 |

Table 4
Radon emanation rate and emanation coefficient (REC) as a function of temperature, grain size and medium entered[a]

| Sample | Grain size (mm) | Temperature (°C) | Time (days) | $^{226}$Ra (dpm g$^{-1}$) | Mean emanation rate (atoms g$^{-1}$ m$^{-1}$) | Mean emanation coefficient (%) |
|---|---|---|---|---|---|---|
| Monazite | o 63 | RT | 7.05–10.99 | 1058 ± 22 | 21.7 ± 0.3[b] | 2.05 ± 0.03 |
| | | RT/Fluid | 16.94 | 1058 ± 22 | 44.1 ± 0.1 | 4.17 ± 0.09 |
| | | 100 | 8.00–12.90 | 1058 ± 22 | 9.49 ± 0.07[b] | 0.90 ± 0.02 |
| | | 200 | 9.01–12.98 | 1058 ± 22 | 11.7 ± 0.1[b] | 1.11 ± 0.02 |
| | | 200/Fluid | 16.94 | 1058 ± 22 | 26.6 ± 0.1 | 2.51 ± 0.05 |
| | | 600 | 5.89–7.02 | 1058 ± 22 | 6.98 ± 0.10[b] | 0.66 ± 0.01 |
| | | 600/Fluid | 16.933 | 1058 ± 22 | 43.6 ± 0.1 | 4.12 ± 0.09 |
| | 1000–2000 | RT | 7.98–9.02 | 1058 ± 22 | 10.4 ± 0.2[b] | 0.98 ± 0.02 |
| | | 100 | 8.83–12.09 | 1058 ± 22 | 8.66 ± 0.06[b] | 0.82 ± 0.01 |
| | | 200 | 11.98–13.0 | 1058 ± 22 | 5.27 ± 0.07[b] | 0.50 ± 0.01 |
| | | 600 | 7.08–10.89 | 1058 ± 22 | 3.11 ± 0.06[b] | 0.29 ± 0.01 |
| Zircon | o 63 | RT | 6.94–10.94 | 300 ± 28 | 31.4 ± 0.2[b] | 1.04 ± 0.01 |
| | | RT/Fluid | 27.91 | 300 ± 28 | 17.7 ± 0.07 | 0.59 ± 0.01 |
| | | 100 | 7.93 | 300 ± 28 | 16.6 ± 0.2 | 0.55 ± 0.01 |
| | | 200 | 6.95–7.99 | 300 ± 28 | 19.2 ± 0.2[b] | 0.64 ± 0.01 |
| | | 200/Fluid | 28.00 | 300 ± 28 | 19.2 ± 0.1 | 0.64 ± 0.01 |
| | | 600 | 8.91–11.96 | 300 ± 28 | 14.1 ± 0.1[b] | 0.47 ± 0.004 |
| | | 600/Fluid | 28.02 | 300 ± 28 | 17.3 ± 0.1 | 0.58 ± 0.01 |
| | 1000–2000 | RT | 6.94–13.08 | 300 ± 28 | 14.1 ± 0.1[b] | 0.47 ± 0.01 |
| | | 600 | 7.08–10.89 | 300 ± 28 | 13.87 ± 0.2[b] | 0.46 ± 0.01 |
| Uraninite | o 63 | RT | 6.98–13.0 | 349,740 ± 4150 | 1842 ± 4[b] | 0.53 ± 0.01 |
| | | 100 | 6.94–10.94 | 349,740 ± 4150 | 1756 ± 4[b] | 0.50 ± 0.01 |
| | | 200 | 6.08–8.97 | 349,740 ± 4150 | 2668 ± 5[b] | 0.76 ± 0.01 |
| | | 600 | 9.93–14.97 | 349,740 ± 4150 | 1053 ± 2[b] | 0.30 ± 0.003 |
| | 1000–2000 | RT | 6.99–13.01 | 349,740 ± 4150 | 1860 ± 5[b] | 0.53 ± 0.01 |
| Thorite | o 63 | RT | 28.0 | 6263 ± 95 | 336.7 ± 1.0 | 5.38 ± 0.08 |
| | | RT/Fluid | 17.82 | 6263 ± 95 | 935 ± 2 | 14.9 ± 0.2 |
| | | 200 | 23.87 | 6263 ± 95 | 150.0 ± 0.6 | 2.39 ± 0.04 |
| | | 200/Fluid | 20.12 | 6263 ± 95 | 1410 ± 4 | 22.5 ± 0.3 |
| | | 600 | 21.85 | 6263 ± 95 | 84.3 ± 0.4 | 1.34 ± 0.02 |
| | | 600/Fluid | 17.83 | 6263 ± 95 | 1483 ± 4 | 23.7 ± 0.4 |
| Cerite | o 63 | RT/Fluid | 9.93 | 2563 ± 30 | 430 ± 1 | 16.8 ± 0.2 |
| | | 200/Fluid | 9.93 | 2563 ± 30 | 588 ± 1 | 22.9 ± 0.3 |
| | | 600/Fluid | 9.91 | 2563 ± 30 | 483 ± 1 | 18.9 ± 0.3 |

[a] 0.1 M HNO$_3$ was used as the fluid medium.
[b] Multiple analyses were conducted and the mean of the values is reported.

mineral monazite shows variation in the REC with grain size and this variation remains similar in both annealed and unannealed minerals; however, in 1–2 mm grain size zircons, the REC values remain the same for both annealed and unannealed minerals; and (4) Zircon shows the least amount of variation in the REC value when compared at different degrees of heating.

The four major mechanisms which have been proposed to explain the release rates of $^{222}$Rn are: (a) diffusion of radon through the solid phase, particularly through a network of nanometer-sized interconnected pore spaces (e.g. Rama and Moore, 1984, 1990); (b) alpha recoil from the decay of $^{226}$Ra resulting in the direct release of $^{222}$Rn from the outer 20 nm of a grain, implying that on a spherical grain of o 40 nm diameter all the $^{222}$Rn will escape the mineral grain (Kigoshi, 1971); (c) release of $^{222}$Rn by diffusion out of the recoil tracks within the mineral. In minerals that are b 40 nm in diameter, Rn isotopes from the deeper regions of the crystals are unavailable for release without the development of a larger internal surface area, such as may result from chemical erosion, weathering or intensive fracturing on a microscopic scale or pathways created by the radiation damage. The track density is characterized by the a-decay dose (D; a-decay events/mg) that is calculated from the concentrations of U and Th as follows (e.g., Murakami et al., 1991):

$$D = 8N_1 (\exp(\lambda_1 t) - 1) + 7N_2 (\exp(\lambda_2 t) - 1)$$
$$+ 6N_3 (\exp(\lambda_3 t) - 1) \qquad (3.1)$$

Table 5

Comparison of REC values for emanation into gas or liquid before and after heating the minerals

|  | Monazite | Zircon | Thorite | Uraninite | Cerite |
|---|---|---|---|---|---|
| REC % (gas) |  |  |  |  |  |
| 25 C | 2.05 | 1.04 | 5.38 | 0.53 | N D |
| 100 C | 0.9 | 0.55 | N D | 0.5 | N D |
| 200 C | 1.11 | 0.64 | 2.39 | 0.76 | N D |
| 600 C | 0.66 | 0.47 | 1.34 | 0.3 | N D |
|  |  |  |  |  |  |
| Ratio (gas) |  |  |  |  |  |
| 100/25 C | 0.44 | 0.53 | — | 0.94 | — |
| 200/25 C | 0.54 | 0.62 | 0.44 | 1.43 | — |
| 600/25 C | 0.32 | 0.45 | 0.25 | 0.57 | — |
|  |  |  |  |  |  |
| REC % (liquid) |  |  |  |  |  |
| 25 C | 4.17 | 0.59 | 14.9 | ND | 16.8 |
| 200 C | 2.51 | 0.64 | 22.5 | ND | 22.9 |
| 600 C | 4.12 | 0.58 | 23.7 | ND | 18.9 |
|  |  |  |  |  |  |
| Ratio (liquid) |  |  |  |  |  |
| 200/25 C | 0.60 | 1.08 | 1.51 | — | 1.36 |
| 600/25 C | 0.99 | 0.98 | 1.59 | — | 1.13 |
|  |  |  |  |  |  |
| Ratio (gas/liquid) |  |  |  |  |  |
| 25 C | 0.49 | 1.76 | 0.36 | — | — |
| 200 C | 0.44 | 1 | 0.11 | — | — |
| 600 C | 0.16 | 0.81 | 0.06 | — | — |

where $N_1$, $N_2$ and $N_3$ are the present numbers of $^{238}U$, $^{235}U$, and $^{232}Th$, respectively, in atoms/mg; $I_1$, $I_2$ and $I_3$ are the decay constants for $^{238}U$, $^{235}U$, and $^{232}Th$, respectively (years$^{-1}$) and 't' is the age of the mineral. $N_2$ is assumed to be equal to $(1/137.88)N_1$ based on natural abundances. This dose calculation assumes a closed system (i.e. negligible loss of daughter nuclides due to recoil and chemical effects). The details on the ages of these minerals and the U and Th concentrations in these minerals are given in Garver (2003). Although there is no relationship between a-decay dose (Table 6) and the radon leakage rates, for zircon and monazite the ratio of the radon emanation coefficient to the a-decay dose remains constant, as compared to the other three minerals; and (d) increased release of $^{222}Rn$ from minerals that have greater surface area (smaller grain size) for the mineral monazite.

The most fundamental reason we see a decrease in the REC value when a mineral is heated is the permanent changes (or at least quasi-permanent over a time scale greater than the experimental time scale) that take place affecting the internal tracks within the mineral. At 100 C, many of the recoil tracks within the mineral are altered leading to a decrease in the release of radon, although the exact mechanism remains unknown. On minerals heated to 200 C, the recoil tracks appear to become widened leading to a freer pathway (perhaps similar to the superconductivity below critical temperature, $T_c$, in certain types of materials) for the release of radon and resulting in the observed increase in the REC value. It is not clear to us as to the factor(s) that causes this reversal of effects between 100 C and 200 C, and thus needs further investigation. Exceeding this temperature, a major portion of the nuclear tracks becomes completely annealed and therefore the radon atoms lose the major conduit of travel out of the grain. This is seen by the significant decrease in the REC values for all minerals after having been heated to 600 C. Overall, the decrease in REC values for zircon is significantly lower compared to other minerals. It is well known that U and Th are heterogeneously distributed in zircon and monazite and thus the heating does not significantly affect its release.

Because all of the minerals (except zircon and monazite) chosen for this analysis are U-and Th-rich minerals, it is reasonable to assume that the radium distribution within these minerals is homogenous. We hypothesize that in minerals such as these where radium is uniformly distributed (as opposed to the distribution in common rocks where most U–Th resides in accessory minerals, adsorbed to clay minerals or occluded in fine-grained cements and other coatings), a major portion of the radon released is via the conduit pathways created by nuclear tracks. In addition, the radiation damage caused by the decay of the alpha-emitting radionuclides within a mineral may result in a mosaic of alpha-recoil track channels along which the mineral can be altered to increase the fraction of diffusion and indirect recoil of U–Th series nuclides. The effects of alpha-decay damage also include increased susceptibility to dissolution and chemical diffusion, decrease in mineral density, etc. (summarized in Murakami et al., 1991). Depending on the crystalline structure and bonding strength between atoms, the extent of radiation damage can cause the mineral to become metamict, particularly in zircon. In metamict minerals, the internal porosity will be higher and hence the RECs are expected to be higher, as REC and internal porosity are linearly related (Tanner, 1980). Murakami et al. (1991) showed that zircon density decreases as radiation damage accumulates. Density is lowest (and hence internal porosity highest) in metamict minerals and thus, $^{222}Rn$ can more easily diffuse through the pores in grains with higher internal porosity.

3.2. Radon Emanation in Solution

Release rates of Rn from minerals placed inside a solution can serve as an analog to a groundwater system. For example, the radon emanation coefficient in 0.1 M $HNO_3$ is expected to be similar to that in groundwater systems, under the assumption that Rn

Table 6
Alpha decay radiation dose the mineral has been subjected to since formation

| Sample | Age $10^9$ years | $^{238}$U dpm g$^{-1}$ | $^{232}$Th dpm g$^{-1}$ | $^{238}$U $\times$ $10^{10}$ atom mg$^{-1}$ | $^{235}$U $\times$ $10^8$ atom mg$^{-1}$ | $^{232}$Th $\times$ $10^{10}$ atom mg$^{-1}$ | Dose[a] $\times$ $10^{11}$ event mg$^{-1}$ |
|---|---|---|---|---|---|---|---|
| Zircon (Brazil) | 2.90 ± 0.2 | 3008 | 461.5 | 1.94 | 1.40 | 0.93 | 1.13 ± 0.12 |
| Monazite | 1.40 ± 0.2 | 1058.5 | 26590 | 0.683 | 0.49 | 53.7 | 2.46 ± 0.36 |
| Thorite | 1.00 ± 0.2 | 6263 | 27243 | 4.04 | 2.91 | 55.0 | 2.25 ± 0.48 |
| Cerite | 1.00 ± 0.2 | 2563 | 913 | 1.65 | 1.19 | 1.84 | 0.29 ± 0.07 |
| Uraninite | 1.00 ± 0.2 | 349741 | 26302 | 226 | 162 | 53.1 | 33.8 ± 7.6 |

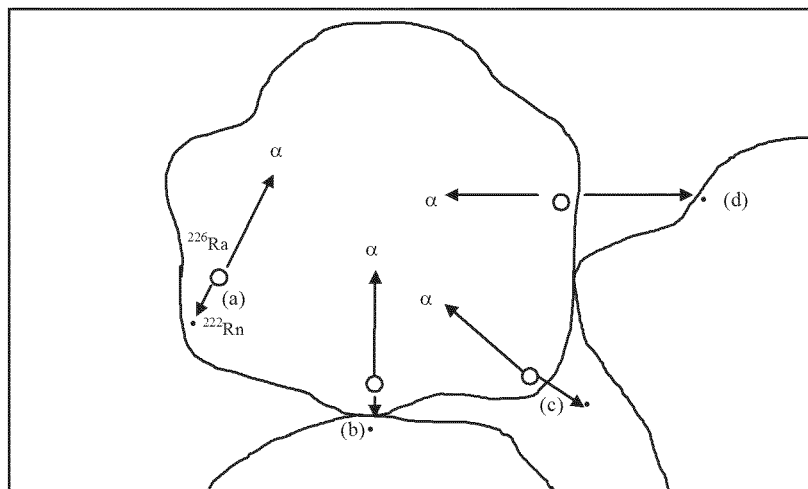[a] The dose was calculated as given in Section 3.1 and Eq. (3.1).



Fig. 1. Potential fate of recoiled $^{222}$Rn atom: ○ represents the $^{226}$Ra atom undergoing alpha decay to produce $^{222}$Rn and • represents the recoiled $^{222}$Rn atom. (a) The $^{226}$Ra atom is located deeper inside the grain than the recoil length and the $^{222}$Rn atom remains embedded in the host grain. (b) The $^{222}$Rn atom is recoiled out of the host grain and gets embedded in an adjacent grain. (c) The $^{222}$Rn atom enters a liquid medium and its recoil energy is absorbed, decreasing the recoil length and leaving the $^{222}$Rn atom free to diffuse in the fluid. (d) The $^{222}$Rn atom travels through void space filled with gas retaining its energy and ultimately embedding itself in a nearby grain (Modified from Tanner, 1978).

release due to dissolution is negligible. In general, there are four locations in which a recoiled $^{222}$Rn atom can reside (Fig. 1). By comparing the release rates of $^{222}$Rn in air and solution, one can determine how much of the radon embeds into adjacent grains and/or lodges into the opposite side of a pore. It has been proposed that inside a natural crystalline mineral there are large internal, interconnected openings that form an extensive network, and solution can enter this network. The openings are basically nanometer channels and it is assumed that water would readily fill those channels. Because the physics of flow at that scale might be quite complex, this assumption also needs to be verified. From the data in Tables 4 and 5, the following observations can be made: (1) Distinctly higher values of REC were found in the solution as compared to air at 25 C, 200 C and 600 C for all the minerals except zircon (at 25 C and 200 C). The diffusion coefficient of radon in air $\approx 0.1\ cm^2\ s^{-1}$, while in water it is $\approx 10^{-5}\ cm^2\ s^{-1}$ and thus the diffusion length in a liquid is $\approx 100$ times smaller than in air. If solution is present in the free space of the material (pore, micropore, crack), the probability that radon-isotopes will terminate their recoil paths in those spaces is high, thus augmenting the direct-recoil fraction. The difference in the REC values between the solution and air can be attributed to the amount of

recoiled $^{222}$Rn that gets embedded into the adjacent grains, which appears to be quite substantial; alternately, if the solution can enter the free space of a mineral grain, when a $^{222}$Rn atom undergoes recoil it may lodge in the opposite wall of the pore. Presence of liquid in the pore will enable the $^{222}$Rn atom to reach the solution; (2) the variation of heating history has a much more profound effect for the REC values in air than it does for the REC values in solution for all minerals. The percentage decrease in the REC with heating ranges from 55–75% for emanation in air, but only 10–40% for emanation into liquid, suggesting that chemical processes such as dissolution and/or leaching are taking place in the presence of solution.

Comparison of the REC values (both in air and liquid) obtained for the monazite samples at 25 C and after heating at 200 C, suggest the following: (a) it appears that about 50% of the $^{222}$Rn recoiled into the solution would get embedded onto adjacent grains in air; and (b) in the monazite sample that was heated at 600 C, only B 15% of the $^{222}$Rn recoiled into the solution would be released into air and 85% would be embedded into adjacent grains. We speculate that heating a mineral results in the creation of new channels and/or widening of existing channels for fluid to enter, thereby enhancing the Rn emanation rate into solution; (3) In zircon, the REC values in the solution at different pre-treatment temperatures remained fairly constant while the REC value at 25 C decreased in solution compared to air. Thus, the amount of recoiled $^{222}$Rn getting embedded onto adjacent grains appears to be very small. It has been shown that monazite remains crystalline even at high concentrations of U and Th. Of the four minerals studied, zircon has the lowest range of REC values even at higher temperatures, indicating that the radon loss from zircon is very small. This is likely due to the difference between the location of U and Th in zircon and other minerals. This validates the extensive application of U–Th–Pb chronology on individual zircon crystals, as the differences in ages calculated between $^{238}$U–$^{206}$Pb, $^{235}$U–$^{207}$Pb and $^{232}$Th–$^{208}$Pb pairs due to radon loss are likely to be negligible; 4) The REC values in cerite in the solution remain constant at all three temperatures (within B 30%).

In summary, the higher REC values in solution compared to air in all three temperatures indicate that a relatively large portion of $^{222}$Rn released from a mineral grain can reach adjacent mineral grains in the absence of liquid and thus, we find very high-REC values in the solution. For the three minerals (thorite, zircon and monazite) for which REC values were determined both in liquid and air, all three minerals exhibited the same temperature trends in REC into air, while none had the same trends in solution. In fact, none of the four minerals examined for REC into solution showed the same trend as another. This suggests the importance of the individual mineral structures, possibly as a result of differing amounts of radiation damage, in the presence of solution in the pore spaces to the resulting value of REC. The overall differences between various minerals are attributed to the differences in the mineral structure and bonding energy between various atoms within the crystal.

## 4. Conclusion

(1) The radon emanation coefficient (REC) for release into air is highest for all unheated minerals, and lowest for all minerals after heating to 600 C. We hypothesize that recoil and alpha-recoil tracks serve as conduit pathways for release of $^{222}$Rn.

(2) The REC is distinctly higher for emanation into solution versus air for monazite and thorite, but relatively constant for zircon, indicating the strong ability of liquid in the pore spaces to prevent the recoiling atom from entering a neighboring grain and/or solution reaching the pore spaces within a grain, and also indicating the importance of the specific characteristics of each mineral in terms of the probability that the recoiling $^{222}$Rn atom will embed itself in an adjacent grain.

(3) The variation of heating history has a much more profound effect on the REC values for emanation into air than it does for emanation into fluid for all minerals. The percentage decrease (on heating) in REC ranges from 55–75% for release into air, but only 10–40% for release into solution. In addition, for the minerals which had the REC determined for release into both air and solution, all exhibited the same trends in REC into air with varying degrees of heating, however, none showed the same trends in solution. These two observations may suggest the importance of chemical processes such as dissolution or leaching taking place in the presence of solution that could contribute varying amounts of Rn to the overall REC value.

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